6th International Symposium on Recent Advances in Food Analysis
November 5 - 8, 2013 - Prague, Czech Republic

FROM GC-MS TO GC-MS/MS TRIPLE QUADRUPOLE ANALYSIS OF NDL PCBs IN FOOD: REDUCED CLEAN-UP AND INCREASED SENSITIVITY

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Introduction

Commission Regulation (EU) 1259/2011 set for the first time maximum levels for non dioxin-like PCBs (NDL-PCBs) in foodstuffs. Six are the PCB congeners (28, 52, 101, 138, 153 and 180) identified as indicators to assess the human exposure upon food consumption. Their sum accounts for about half of the NDL-PCBs contamination in food. Laboratories in charge of official control are requested to monitor these contaminants in food and feed and check the compliance to regulatory limits. The limits in force are not very strict because of the too high LOQs of the EU laboratories yield to PCB-sums, in the u.b. approach, very close to the maximum levels even if no congener is quantified. Therefore the Regulation (EU) 1259/2011 itself strongly recommend to enhance the sensitivity of the analytical methods because a revision of the maximum levels is foreseen in three years time. Here we present the evolution of the analytical procedure adopted in our laboratory. The GC-MS method for the determination of the 6-indicator-PCBs was already fast and high trough-put, but, upon installation of a new GC-MS TRIPLE QUAD some changes were made to the procedure. The highest sensitivity of the new instrument enabled a reduction of the clean-up steps, simplifying the sample preparation, and the lowering of the limit of quantification of the method to 0.5 ng/g fat.

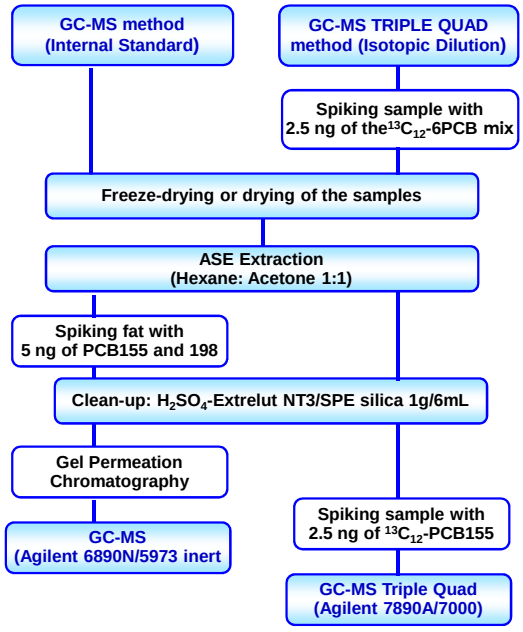

Figure 1 *- Flow diagram of sample preparation*

GC-MS Method

- **Column**: SGE-HT8 PCB capillary column (60m x 0.25mm x 0.25µm)
- **Oven temperature program**: 120°C, ramp to 200°C at 20°C/min, ramp to 270°C at 3°C/min, ramp to 300°C at 15°C/min, hold 4.67 mins.
- **Temperatures**: transfer line 280°C, source 230°C, quadrupoles 150°C
- **Injector**: split-splitless, T=270°C.
- **Injection mode**: 1 µL in pulsed splitless, inj. pulse pressure 30 psi, purge flow 40 mL/min.

Method verification

The methods performances were verified assessing the repeatability on spiked samples of different matrices (milk, eggs, muscle) at the LOQ=0.5 ng/g fat (n=7). The specificity was assessed doing repeated analysis (n=7) on the same blank matrices. Stored aliquots of samples dispatched from the EURL for Dioxins and PCBs in Feed and Food in the frame of European Proficiency Test exercises were also re-analysed with the GC-MS triple quad method.

Table 1 *– Ion selected for the GC methods*

	GC-MS		GC-MS Triple Quad		
	Monitored Ions(m/z)		Monitored Transitions (m/z)		
	Target	Qualifiers	Precursor ion	Product ion	CE
PCB28	256	258, 260, 186	257.8	186	32
			255.8	186	32
			185.9	151	26
PCB52	292	290, 255, 220	291.8	222	32
			289.8	220	38
			219.8	150	42
PCB101	326	328, 256, 254	327.7	256	32
			325.7	256	32
			253.8	184	40
PCB153	360	362, 290, 288	361.6	290	36
			359.7	290	36
			289.8	218	42
PCB138	360	362, 290, 288	361.6	290	32
			359.7	290	42
			289.8	218	42
PCB180	394	396, 324, 398	395.7	324	36
			393.6	324	36
			323.7	254	43
PCB155	360	362, 290, 288			
PCB198	430	428, 393, 360			
PCB28-L			267.9	198	32
PCB52-L			301.8	232	33
PCB101-L			337.8	268	33
PCB153-L			371.8	302	33
PCB138-L			371.8	302	35
PCB180-L			405.7	335.9	35
PCB155-L			371.8	301.9	34

Results and discussion

The developed GC-MS/MS procedure resulted faster and more sensitive than the former GC-MS method enabling the simultaneous analysis of several samples in the same batch by a single operator.The cut out of the GPC clean-up shortened the sample preparation. The introduction of the six $^{13}C_{12}$ analogues of the six PCBs and of the $^{13}C_{12}$-PCB155 as syringe standard as well as the lowering of the LOQ at 0.5 ng/g fat improved the quantification and the quality control of the procedure. Good specificity, recoveries and repeatability were obtained for the three matrices tested doing replicate analysis on blank and spiked samples (Table 2). Lower recoveries were obtained for PCB 101 and 153 in milk. The trueness was determined spiking the six PCB congeners on a presumably blank matrix, but the milk turned out to have concentration of PCB101 (0.5ng/g fat) and PCB153 (1.0 ng/g fat) comparable or higher than the spiking level. Good repeatability were anyway obtained.

The revised method was also tested analysing again stored aliquots of samples dispatched from the European Reference Laboratory for Dioxins and PCBs in Feed and Food in the frame of European Proficiency Test exercises (2010: milk fat and pork fat; 2011: fish oil; 2012: lard, whole egg and yolk). The results obtained were in good agreement with the PTs consensus values: maximum deviation of 23% for the single congeners and of 18% for the u.b. sum of the six PCBs were obtained doing duplicate analysis of each of the six PT materials.

Table 2 *– Method verification: spiking levels, mean concentrations, recoveries (R %) and coefficients of variation obtained in repeatibility (CV_r%) conditions for both the GC-MS and the GC-MS/MS methods.*

	GC-MS method (Internal standard)						GC-MS triple quad method (Isotopic Dilution)					
Spiking Level *LOQ*	1.0 ng/g fat						0.5 ng/g fat					
PCB	28	52	101	153	138	180	28	52	101	153	138	180
MUSCLE												
Mean (ng/g fat)	1.1	0.8	0.9	0.5	1.0	1.0	0.4	0.5	0.5	0.6	0.6	0.5
R%	120	93	99	60	109	106	88	93	101	113	103	96
CVr (%)	16	10	8	33	13	15	5	5	3	11	7	4
EGGS												
Mean (ng/g fat)	0.8	1.0	1.1	1.1	0.9	0.6	0.3	0.5	0.4	0.5	0.5	0.4
R%	72	84	93	98	83	52	76	112	89	104	101	81
CVr (%)	9	8	7	18	17	35	4	3	4	5	4	4
MILK												
Mean (ng/g fat)	0.8	0.8	1.1	0.5	1.1	0.9	0.5	0.4	0.2	0.2	0.4	0.5
R%	77	73	106	44	102	88	95	77	40	52	82	104
CVr (%)	23	2	11	33	14	9	5	9	17	23	10	5

Table 3 *– Comparison of EUPTs results obtained using GC-MS and GC-MS/MS methods.*

	EUPT RESULTS (ng/g fat)					
	GC-MS	ASSIGNED VALUE	GC-MS triple quad	GC-MS	ASSIGNED VALUE	GC-MS triple quad
	Milk Fat *(2010)*			Pig Fat *(2010)*		
28	4.0	6.5	5.6	1.2	2.2	2.2
52	12.9	15.4	13.9	2.5	2.1	2.2
101	10.0	10.8	9.3	2.2	1.9	1.8
153	7.3	5.3	4.1	2.3	1.3	1.3
138	5.1	6.2	4.8	2.2	1.4	1.3
180	2.4	2.4	2.4	3.2	2.9	2.9
ΣPCB *u.b.*	41.7	48.6	39.9	13.6	11.8	11.8
ΣPCB *l.b.*	41.7	48.5	39.9	13.6	12.1	11.8
	Fish Oil *(2011)*			Lard *(2012)*		
28	1.0	not assigned	0.6	1.1	1.7	1.6
52	1.6	2.0	2.0	6.8	8.8	8.4
101	5.7	5.6	4.6	9.2	9.0	8.3
153	15.0	12.9	11.1	6.3	4.8	3.9
138	9.8	9.5	7.3	7.4	5.6	4.8
180	3.6	3.8	3.5	3.5	3.7	3.2
ΣPCB *u.b.*	37.0	35.0	29.2	34.1	34.3	30.2
ΣPCB *l.b.*	36.0	34.4	29.2	34.1	34.0	30.2
	Whole Eggs *(2012)*			EggsYolk *(2012)*		
28	<1	not assigned	<0,5	6.9	8.6	7.7
52	<1	not assigned	<0,5	14.0	15.7	15.0
101	<1	not assigned	<0,5	8.6	9.3	8.3
153	4.6	4.3	3.8	4.7	4.4	4.2
138	3.8	3.7	3.8	5.2	5.1	4.2
180	2.9	2.9	3.2	2.6	2.6	2.7
ΣPCB *u.b.*	14.3	11.8	12.2	41.8	46.7	42.0
ΣPCB *l.b.*	11.3	11.2	10.7	41.8	46.7	42.0

Conclusions

The introduction of the GC-MS triple quad for the analysis of indicators PCB fulfils the request of the EU Regulation of lowering the LOQs of the method in order to respond to a future modification of the permitted maximum levels.

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Stampato a cura dell'Unità Operativa di Supporto Biblioteca, Informazione, Editoria (2011).